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Molten Lithium Sulfate-Sodium Sulfate-Potassium Sulfate Eutectic: Reactions of Some Sulfur Compounds

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The reactions of sulfide and of five sulfur oxyanion salts (Na_2SO_3, $Na_2S_2O_5$, $K_2S_2O_5$, $Na_2S_2O_3$, and $K_2S_2O_7$) were studied by themselves and in the molten ternary sulfate eutectic under nitrogen, with air, sulfur dioxide, sulfur trioxide, and carbon dioxide, and with acidic, basic, and reducing solutes. The sulfur-containing products were elemental sulfur and sulfate though sulfur oxides were sometimes evolved and a number of intermediates formed. Reaction products were identified qualitatively and quantitatively, often by TGA, and reaction schemes are suggested.

Introduction

The chemistry of sulfur compounds in molten sulfates is of great practical importance. For example, all sulfuric acid is manufactured by catalytic aerial oxidation of sulfur dioxide using a molten sulfate solution containing vanadium and often other transition metals, while the corrosion of the steel surfaces of high-temperature boilers and heat exchangers has been shown to be controlled by the transport of reactants and products through the molten sulfate film that is formed on these surfaces.

Despite this importance, studies of the chemistry of sulfur compounds in molten sulfates are few and often very incomplete. Currently, phase-diagram studies of sulfides with sulfates have been reported,[1,2] suggesting stability, and, in an aside, suggestions made as to the products of sulfide and sulfite reacting in sulfate-pyrosulfate eutectic.[3] Sulfite in molten sulfate has been reported to form sulfur dioxide[4] and also sulfur plus sulfur dioxide.[5] The blue solution that sulfur can form in molten sulfate has been linked to more substantial studies of similar solutions in other molten salts by Giggenbach.[6] Sulfur trioxide has been claimed to have "negligible solubility" in sulfate melts,[4] while, in a recent study,[7] Hansen et al. report on the solubility of K_2SO_4 in $K_2S_2O_7$ from 410 to 450 °C. In view of this scarcity of quantitative information, a number of sulfur compounds were studied in molten ternary sulfate eutectics as part of a wider study of the sulfate-vanadium solutions used in sulfuric acid manufacture.

Experimental Section

Materials. The ternary eutectic (78 mol % Li_2SO_4, 8.5 mol % Na_2SO_4, 13.5 mol % K_2SO_4, mp 512 °C) was prepared from appropriate amounts of the AnalaR sulfates (BDH), previously dried separately at 200 °C for 2 h. After being thoroughly mixed, the sulfates were fused in a silica breaker, placed in a muffle furnace at 650 °C, then poured into a porcelain dish, and cooled in a desiccator. Before use the eutectic was finely ground and heated to 200 °C for 2 h. Acidimetric titration of aqueous solutions indicated that the melts contained residual oxide in the range 0.04-0.06 *m*, which could be neutralized by addition of the appropriate quantity of potassium pyrosulfate.

Sodium sulfide (BDH, $Na_2S{\cdot}9H_2O$) was dried over concentrated sulfuric acid in a vacuum desiccator for 2 weeks and then in vacuo at 200 °C for 3 h and, though impure, was used to give qualitative information on reactions. Sodium chloride and sodium carbonate (AnalaR) were dried at 110 °C for 2 h. Sodium metabisulfite (reagent grade) and potassium metabisulfite (AnalaR) were dried at 110 °C for 1 h. Sodium thiosulfate (AnalaR), vanadium pentoxide, and sodium sulfite (reagent grades) were dried for 2 h at 110 °C and analyzed. Anal. Calcd for $Na_2S_2O_3$: $S_2O_3^{2-}$, 70.8. Found: $S_2O_3^{2-}$, 70.6. Calcd for V_2O_5: V, 56.0. Found: V, 55.5. Calcd for Na_2SO_3: SO_3^{2-}, 63.5. Found: SO_3^{2-}, 61.0. Potassium pyrosulfate was prepared by heating potassium persulfate (AnalaR) at 220 °C for 4 h[8] and then was stored in a desiccator. The product gave no blue color with starch-iodide, but titration of aqueous solutions with sodium hydroxide showed 64.4% $S_2O_7^{2-}$ (calcd for $K_2S_2O_7$ 65.2%).

Air was drawn from a BOC compressed-air cylinder and then passed through potassium hydroxide and concentrated sulfuric acid wash bottles and a phosphorus pentoxide drying tube. The flow rate was monitored with a GAP flowmeter. Nitrogen (BOC oxygen free) and carbon dioxide were passed through a chromium(II) bubbler before being dried and monitored in the same way. Sulfur dioxide (BOC anhydrous 99.8% grade) was used without further purification. Sulfur trioxide was produced by passing a mixture of air (94%) and sulfur dioxide (6% volume) through a Pyrex tube filled with commercial catalyst pellets (ISC Chemicals Ltd.) held in a furnace at 420 °C, 98% conversion being achieved.

Procedure. Qualitative reactions were carried out in tubes heated by an electrical-resistance furnace controlled by an Ether Transitrol Controller (Type 991) with provision for supply of different gas atmospheres. The usual temperature for study was 580 °C when Pyrex was used as a container material, but above 600 °C, silica was substituted. Reagents either were well mixed with the finely powdered eutectic at room temperature or were added at temperature via a bent side arm. Quantitative investigations were carried out on a Stanton TR-1 thermobalance with use of a pure gold crucible (10 mL, Johnson-Matthey Grade 2) and a heating rate of 2°/min, unless otherwise stated. A water-cooled baffle-plate attachment was fitted (Stanton-Redcroft, No. 8726) so that thermogravimetry could also be carried out under poisonous and/or corrosive atmospheres. Weight changes, the average of three or more determinations, are reported as a percentage of the weight of the initial reactant.

Products were identified by conventional tests on the gas effluent or on aqueous solutions made from solidified reacted melts. For sulfur anions, a neutral solution was shaken with a cadmium carbonate suspension. Treatment of the resulting precipitate with dilute sulfuric acid gave hydrogen sulfide (if sulfide was present) or hydrogen sulfide plus insoluble sulfur (for polysulfide). Strontium nitrate solution added to the resulting filtrate precipitated sulfate and/or sulfite, the latter being identified by evolution of sulfur dioxide on treatment with acid. The remaining filtrate was tested for thiosulfate by adding hydrochloric acid. Evolution of sulfur dioxide and precipitation of sulfur indicated the presence of thiosulfate. Quantitatively, the total sulfite plus sulfide was determined after solution of the quenched melt in deoxygenated water under a nitrogen atmosphere by addition of a known amount of iodine followed by titration of the excess with thiosulfate. Sulfide alone was then determined by titration with potassium ferricyanide using ferrous dimethylglyoxime indicator, after precipitation of sulfite and sulfate with barium chloride solution. Sulfite was then determined by difference. Nickel was estimated gravimetrically by precipitation with dimethylglyoxime.

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Table I. Reaction of Sodium Chloride with Potassium Pyrosulfate in Li_2SO_4-Na_2SO_4-K_2SO_4 Eutectic (3 g) under Nitrogen

expt	mmol of NaCl	mmol of $K_2S_2O_7$	mole ratio	wt loss (300-750 °C), mg	mmol of unreacted Cl^-	ratio of reacted Cl^-:$K_2S_2O_7$
1a	6.51	3.91	1.66:1	266	2.9	0.92:1
1b	9.59	3.29	2.92:1	241	7.95	0.50:1
1c	16.54	5.09	3.23:1	320	9.93	1.28:1
1d	17.59	3.47	5.07:1	224	13.40	1.21:1

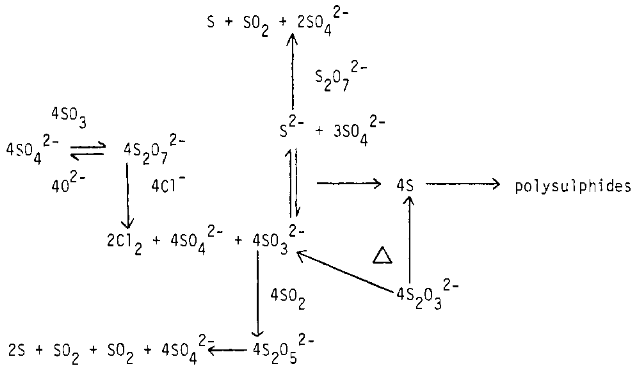

Figure 1. Survey of reactions of sulfur species in the ternary sulfate eutectic.

Some solid products were identified by X-ray powder diffraction using a Phillips (Eindhoven) diffractometer and nickel-filtered Cu Kα radiation. The *d* spacings and intensities were matched with those of known compounds from the ASTM index.

Results and Discussion

The results are subdivided according to the sulfur species under investigation. Some overlap is inevitable although the order follows a logical progression. A general survey of reactions of sulfur species in the sulfate eutectic is given in Figure 1.

Pyrosulfate. Thermogravimetric analysis of potassium pyrosulfate in ternary eutectic under nitrogen is illustrated in Figure 2, curve A. Weight loss began at 350 °C, being complete at 650 °C and corresponding to 31.0%, calculated for that of

$$S_2O_7^{2-} \rightarrow SO_4^{2-} + SO_3 \qquad (1)$$

being 31.5%. The lower temperature of decomposition compared to that reported for potassium pyrosulfate alone was undoubtedly due to the small acidic lithium cation present in the ternary eutectic. In a sulfur trioxide atmosphere (6% SO_3, 94% air), acidimetric titration of ternary eutectic showed a sulfur trioxide solubility of 0.0067 ± 0.005 *m* at 580 °C, with saturation being reached in less than 2 h, suggesting that the earlier finding[4] of "negligible solubility" was likely to have been caused by a near-zero partial pressure. Hansen et al.[7] suggest that at 430 °C pyrosulfate may in fact decompose, giving $S_3O_{10}^{2-}$ and SO_4^{2-} rather than SO_3 and SO_4^{2-}. This may well be true under positive partial pressures of SO_3, as the above acidimetric titration suggests, but under dynamic nitrogen atmospheres eq 1 will become important.

The addition of pyrosulfate to the melt at 600 °C containing dissolved sodium chloride resulted in evolution of large quantities of sulfur trioxide along with chlorine, sulfur, and sulfur dioxide.

The results of a thermogravimetric study of this system are summarized in Figure 2 and Table I. In each reaction chlorine, sulfur, and sulfur dioxide were detected in the gas effluent. The chloride ion remaining in the quenched melt was determined quantitatively. The simple oxidation-reduction reaction

$$2Cl^- + S_2O_7^{2-} \rightarrow Cl_2 + SO_3^{2-} + SO_4^{2-} \qquad (2)$$

if followed by the reaction of sulfite, or its disproportionation products (see below), with more pyrosulfate (i.e., eq 7 or eq 8 plus 9) gives the overall equation

$$8Cl^- + 6S_2O_7^{2-} \rightarrow 4Cl_2 + S + SO_2 + 10SO_4^{2-} \qquad (3)$$

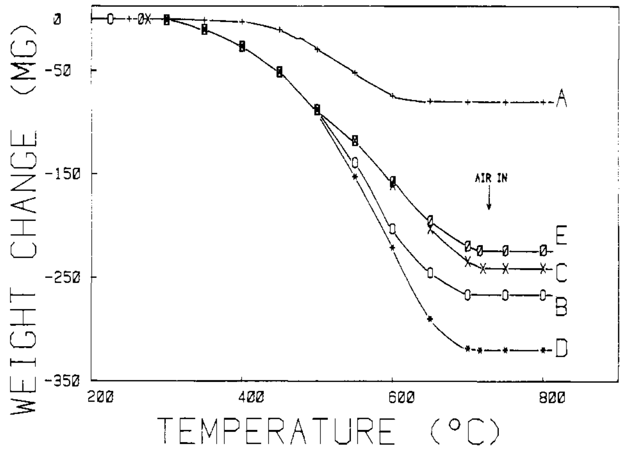

Figure 2. Thermogravimetric analysis of NaCl and $K_2S_2O_7$ in Li_2SO_4-Na_2SO_4-K_2SO_4 eutectic under nitrogen and then air for experiments in Table I: A (+), 1 mol of $K_2S_2O_7$ in 2 g of ternary eutectic; B (○), expt 1a; C (×), expt 1b; D (*), expt 1c; E (⊘), expt 1d.

If this is followed by the decomposition of the remaining excess pyrosulfate as in eq 1, it accounts for all the observed products and also gives weight losses in accord with those observed. However, sulfite is not the usual product of pyrosulfate reduction. A more plausible, but more complex, reaction scheme giving the same products and overall stoichiometry (and hence the same weight losses) is

$$\begin{aligned} &Cl^- + S_2O_7^{2-} \rightarrow SO_4^{2-} + [SO_3Cl^-] \\ &[SO_3Cl^-] \rightarrow {}^1/_2Cl_2 + {}^1/_2[S_2O_6^{2-}] \\ &{}^1/_2[S_2O_6^{2-}] \rightarrow {}^1/_2SO_2 + {}^1/_2SO_4^{2-} \end{aligned} \qquad (4)$$

with the chlorosulfate anion acting as a catalyst for a chloride/sulfur dioxide reaction. I.e.

$$\begin{aligned} &SO_3Cl^- + SO_2 \rightarrow SO_3 + SO_2Cl^- \\ &[SO_2Cl^-] \rightarrow {}^1/_2Cl_2 + {}^1/_2[S_2O_4^{2-}] \\ &{}^1/_2[S_2O_4^{2-}] \rightarrow {}^1/_2S + {}^1/_2SO_4^{2-} \end{aligned} \qquad (5)$$

and

$$SO_3 + Cl^- \rightarrow SO_3Cl^- \qquad (6)$$

since it is known that sodium dithionate ($Na_2S_2O_6$) decomposes to sodium sulfate and sulfur dioxide above 200 °C and that dithionous acid ($H_2S_2O_4$) thermally decomposes in a sealed tube to sulfuric acid and sulfur.[9] The identification of the intermediates actually involved requires further work and may, of course, indicate a somewhat different reaction scheme, but the overall stoichiometries are established below.

The reaction of pyrosulfate with sulfite in the ternary eutectic was studied thermogravimetrically, the results being summarized in Figure 3 and Table II. In each case, under

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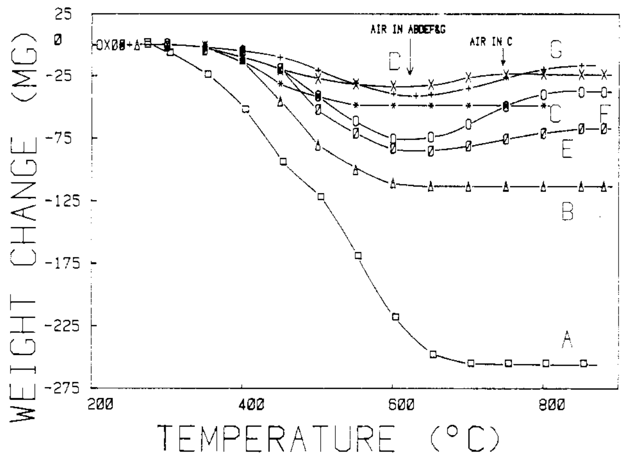

Figure 3. Thermogravimetric analysis of Na_2SO_3 and $K_2S_2O_7$ in Li_2SO_4–Na_2SO_4–K_2SO_4 eutectic under nitrogen and then air for experiments in Table II: A (□), expt 2a; B (△), expt 2b; C (*), expt 2c; D (×), expt 2d; E (⊘), expt 2e; F (○), expt 2f; G (+), expt 2g.

Table II. Reaction of Sodium Sulfite and Potassium Pyrosulfate in Li_2SO_4–Na_2SO_4–K_2SO_4 Eutectic (3 g) under Nitrogen Followed by Air

a. Sample Compositions and Observed Weight Losses

expt	mmol of Na_2SO_3	mmol of $K_2S_2O_7$	mole ratio	wt loss in N_2 (260–650 °C), mg	wt gain in air (above 650 °C), mg
2a	3.54	3.91	0.91:1	256	0
2b	4.15	2.22	1.87:1	112.5	0
2c	2.00[a]	1.00[a]	2.00:1	49.0	0
2d	2.00[a]	0.70[a]	2.86:1	33.5	8
2e	8.04	2.46	3.27:1	86	19
2f	8.07	2.07	3.67:1	75	37
2g	4.05	1.00	4.05:1	40	23

b. Calculated Weight Losses

expt	I[b]	II[c]	III[d]	IV[e]	V[f]
2a		3.54		256.5	
2b		4.15		111.5	
2c		2.00		48.0	
2d	0.5	1.40	0.1	33.6	33.5
2e	1.19	4.92	1.93	118.6	86
2f	2.31	4.14	1.62	99.6	73.7
2g	1.44	2.00	0.61	49	40

[a] In 2 g of ternary eutectic. [b] Excess Na_2SO_3 (calcd from wt gain in air, eq 13) (mmol). [c] Na_2SO_3 reacting with $K_2S_2O_7$ (eq 7 or eq 8 plus eq 9) (mmol). [d] Remaining Na_2SO_3 available to react with SO_2 in situ (mmol). [e] Weight loss (predicted by eq 7, eq 8 plus eq 9, and eq 13) (mg). [f] Weight loss (predicted by eq 7, eq 8 plus eq 9 with eq 10, or eq 8 plus eq 14, for expts 4–7) (mg).

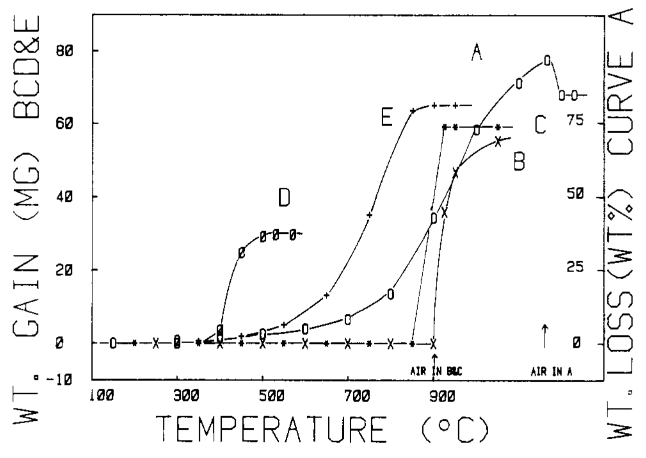

Figure 4. Thermogravimetric analysis of Na_2S and Na_2SO_3 by themselves and in Li_2SO_4–Na_2SO_4–K_2SO_4 eutectic: A (○), Na_2S in melt under nitrogen in a silica crucible; B (×), Na_2SO_3 (1.33 *m*) in 3 g of melt under nitrogen; C (*), Na_2SO_3 (0.50 g) alone under nitrogen; D (⊘), Na_2SO_3 (1.00 *m*) in 2 g of melt in air; E (+), Na_2SO_3 (0.55 g) alone in air.

nitrogen, sulfur and sulfur dioxide were detected in the exit gas. Sulfur trioxide was also detected if the sulfite to pyrosulfate ratio was less than 2:1. This leads us to propose the reaction scheme

$$4SO_3^{2-} + 2S_2O_7^{2-} \rightarrow 4SO_4^{2-} + 2[S_2O_5^{2-}]$$

$$2[S_2O_5^{2-}] \rightarrow S + SO_2 + 2SO_4^{2-} \qquad (7)$$

with excess pyrosulfate decomposing as in (1). It is also possible that sulfide, the disproportionation product of sulfite (see below), reacts with pyrosulfate

$$4SO_3^{2-} \rightarrow S^{2-} + 3SO_4^{2-} \qquad (8)$$

$$S^{2-} + 2S_2O_7^{2-} \rightarrow S + SO_2 + 3SO_4^{2-} \qquad (9)$$

the same overall stoichiometry being established. In addition we propose, for ratios of sulfite to pyrosulfate greater than 2:1, sulfite (or sulfide) may also react with sulfur dioxide produced in situ:

$$SO_3^{2-} + SO_2 \rightarrow [S_2O_5^{2-}] \rightarrow {}^1/_2S + {}^1/_2SO_2 + SO_4^{2-} \qquad (10)$$

This stoichiometry is established by separate experiments below and, as Table II indicates, allows us to account for all the thermogravimetric results.

Sulfide. Sodium sulfide dissolved in the sulfate ternary eutectic at 600 °C, giving a yellow-brown solution under an atmosphere of nitrogen, apparently did not change as on quenching no other oxidizable sulfur species were found by qualitative analysis. Addition of nickel (II) sulfate to these solutions resulted in the formation of a black precipitate, shown to be nickel(II) sulfide by X-ray diffraction ("*d*" values: 2.98 (100), 2.57 (80), 1.98 (100), 1.73 (33). *d* values from ASTM index for NiS: 2.98 (80), 2.58 (70), 1.97 (100), 1.71 (80)). Upon addition of potassium pyrosulfate, the precipitate redissolved, re-forming a rose red solution typical of nickel(II), sulfur and sulfur dioxide being evolved. A black precipitate was also formed on addition of vanadium pentoxide, which redissolved with pyrosulfate, giving turquoise solutions of oxyvanadium(IV) cations, suggesting that sulfide, not unexpectedly, is reducing:

$$V_2O_5 + S^{2-} \rightarrow 2VO_2 + O^{2-} + S \qquad (11)$$

$$VO_2 + S_2O_7^{2-} \rightarrow VOSO_4 + SO_4^{2-} \qquad (12)$$

The reaction tubes were heavily etched, showing the basic nature of sulfide solutions. Thiosilicates ($Na_2S{\cdot}SiO_2$ and $Na_2S{\cdot}2SiO_2$) are formed when silica is heated above 600 °C with sodium sulfide.[10,11]

Reaction of sulfide with silica in sulfate melts is illustrated thermogravimetrically in Figure 4, curve A. Under a nitrogen atmosphere, weight loss was due to evolution of sulfur and sulfur dioxide. Oxidation of unreacted sulfide to sulfate (the only sulfur species detected on quenching) occurred upon introduction of oxygen into the nitrogen stream, a corresponding weight gain being recorded. Similarly, on addition of pyrosulfate to sulfate melts containing sodium sulfide only (at 580 °C under N_2), sulfur and sulfur dioxide were evolved. Shaking the tubes before gaseous evolution was complete re-

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Table III. Disproportionation of Sodium Sulfite in Li_2SO_4-Na_2SO_4-K_2SO_4 Eutectic under Nitrogen

temp, °C	mmol of orig SO_3^{2-}	mmol of SO_3^{2-} after heating	mmol of S^{2-} after heating	mmol of $4[S]^{2-} + [SO_3^{2-}]$ after heating
400	3.95	3.93	0	3.93
450	3.93	3.90	0	3.90
500	3.93	3.71	0.025	3.81
550	3.93	3.49	0.069	3.77
600	3.93	1.06	0.548	3.25

sulted in an intensely blue melt. This result was also obtained upon addition of sulfur directly to sulfide-containing melts. Quenching of the blue melts and subsequent analysis revealed the presence of polysulfide species.

The blue species above is probably similar to that briefly mentioned by Giggenbach[6] and also found in other melt solutions under similar conditions. After some controversy, the coloration was shown conclusively to be due to the trisulfide radical ion in chloride melts.[12]

The stoichiometries of the above reactions were revealed on studying reactions of sulfite and sulfate melts and are covered in the next section.

Sulfite. General Observations. Sodium sulfite was soluble in the ternary eutectic, forming a pale brown solution. At 600 °C, the solubility was more than 0.48 *m* but considerable quantities of sulfide were present, as behavior with vanadium pentoxide and nickel(II) sulfate identical with that described with sodium sulfide was obtained. Thus, 2.26 mmol of nickel(II) sulfate was added to melt containing 4.78 mmol of sodium sulfite, the weight of black precipitate after water extraction and drying corresponded to 1.21 ± 0.01 mmol of nickel(II) sulfide, and the filtrate contained 1.05 ± 0.01 mmol of soluble nickel(II); i.e., the ratio of sulfite added to nickel(II) sulfide to nickel(II) sulfate reacted was 3.96:1:1, supporting the disproportionation in eq 8. The extent of this disproportionation was determined between 400 and 600 °C. A 4-mmol portion of sodium sulfite in ternary eutectic (i.e. 1.3 *m*) was heated in silica crucibles under nitrogen for 3 h to allow equilibration and then analyzed for total reducing sulfur species and sulfide only. The results (Table III) show that disproportionation did not occur until melting began (at ~500 °C) and that the extent increased very greatly between 550 and 600 °C. Considerable amounts of sulfur were lost from the melt at these temperatures as evolved sulfur and sulfur dioxide, probably through the formation of thiosilicates and silicates.[10,11]

The extent of disproportionation (eq 8) was much greater than has been reported for alkali-metal sulfites heated alone[13,14] (i.e. commencing at 650 °C for Li_2SO_3 and 850 °C for K_2SO_3 and not reaching 75% disproportionation until about 800 and 930 °C, respectively) and again may be due to interaction with silica as well as being facilitated by the solubility of reactant and products. In chloride melts this disproportionation has been observed at 500 °C in the presence of metal cations that form insoluble sulfides,[15] while sulfite was in equilibrium with the dissociation products, sulfur dioxide and oxide, in molten nitrates at 300 °C.[16] The formation of sulfide was apparently not noted by Burrows and Hills[4] when they used sulfite dissolved in a binary sulfate eutectic (Li_2SO_4-K_2SO_4) at 625 °C as a source of in situ sulfur dioxide for electrochemical reduction studies.

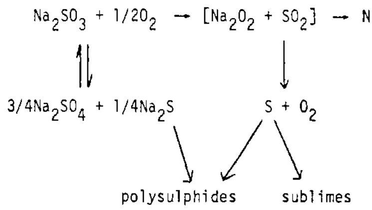

Figure 5. Suggested oxidation products of oxidation of sodium sulfite by air.[15]

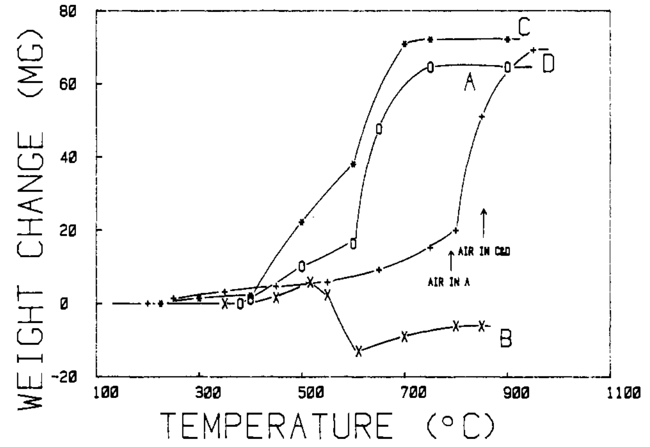

Figure 6. Thermogravimetric analysis of Na_2SO_3 and Na_2CO_3 by themselves and in Li_2SO_4-Na_2SO_4-K_2SO_4 eutectic (3 g) under various atmospheres: A (○), Na_2SO_3 (1.33 *m*) in N_2 (88%)-SO_2 (12%); B (×), Na_2SO_3 (1.73 *m*) in CO_2; C (*), Na_2CO_3 (0.67 *m*) in N_2 (88%)-SO_2 (12%); D (+), Na_2CO_3 (0.21 g) alone in N_2 (88%)-SO_2 (12%).

Thermogravimetric Results. Sodium sulfite was investigated by itself and in the ternary eutectic in nitrogen and air atmospheres. The results are summarized in Figure 4, curves B–E. They show that, in the absence of silica (under N_2 atmospheres), either by itself or with ternary eutectic, sulfite (and therefore sulfide) is stable to decomposition to 900 °C (no weight loss). Introduction of air at 900 °C caused rapid weight gain in both cases. When the samples were heated in air alone or with ternary eutectic (curves D and E), similar overall weight gains were observed, the onset of weight gain occurring at markedly lower temperatures in the presence of the melts. In each case, the total weight gain (11.1, 11.9, 11.98 and 11.9%, respectively) was less than expected from the reaction

$$Na_2SO_3 + {}^1/_2O_2 \rightarrow Na_2SO_4 \qquad \text{calcd wt gain 12.7\%} \qquad (13)$$

and is attributed to a number of other oxidation pathways[17] (Figure 5). This also accounts for the observed byproducts, sulfur in the exit gases and traces of polysulfide in the quenched melts. The increased rate of oxidation above 700 °C of sodium sulfite was attributed by Sack[18] to oxidation of sulfide formed by the disproportionation mechanism. The much lower temperature of this increased rate of oxidation with melt cannot however be attributed to the same cause and must indicate the facilitating effect of a large excess of sulfate or of the alkali-metal cations (probably lithium).

Introduction of sulfur dioxide to the nitrogen flow over sodium sulfite in the sulfate melt resulted in a weight gain (Figure 6, curve A). Sulfur was detected on the effluent gases while sulfate was the only sulfur species detected in the quenched melt. These observations and the overall weight gain (12.7%) are explained by the stoichiometry of eq 10.

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Thus, the proposal above that sulfite may react with sulfur dioxide produced in situ seems to be well supported. In addition, potassium metabisulfite has been reported to decompose in this manner above 200 °C,[19] and the results of an experimental investigation are discussed below. However, in view of the increased disproportionation of sulfite in the eutectic above 580 °C and the increased rate of weight gain above 600 °C, an alternative pathway to eq 10 is also suggested:

$$S^{2-} + 2SO_2 \rightarrow S + [S_2O_4^{2-}] \rightarrow 2S + SO_4^{2-} \qquad (14)$$

The thermogravimetric trace observed in a carbon dioxide atmosphere (Figure 6, curve B) was more complex than the above, a series of weight gains and losses being observed. The quenched melt contained no oxidizable sulfur, and sulfur dioxide was detected in the exit gases. These observations are explained if it is assumed that carbonate was produced via the reaction

$$Na_2SO_3 + CO_2 \rightarrow Na_2CO_3 + SO_2 \qquad (15)$$

while the remaining sulfite reacted with the sulfur dioxide produced in situ as in (10) or (8) plus (14). This resulted in a calculated overall weight loss of 7.1 mg compared to the experimentally observed overall weight loss of 6 mg.

The reverse of reaction 7 was investigated when sodium carbonate (alone and with ternary eutectic) was heated in sulfur dioxide containing atmospheres (Figure 6, curves C and D). In a sulfate environment, two weight-gain regions were observed from 240 to 540 °C and from ~550 to 800 °C, corresponding to the reaction

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

$$\text{wt gain per } Na_2CO_3\text{: calcd, 18.9\%; obsd, 19.3\%} \qquad (16)$$

and summarizing (10) or (8) plus (14)

$$Na_2SO_3 + {}^1/_2SO_2 \rightarrow Na_2SO_4 + {}^1/_2S \qquad (17)$$

$$\text{wt gain per original } Na_2CO_3\text{: calcd, 15.1\%; obsd, 15.1\%}$$

Again, sulfur was observed in the exit gases and no oxidizable sulfur species were found in the quenched melt, supporting these proposed reaction routes. In the absence of sulfate melt (curve D) the overall weight gain was 33.0%, which is close to that expected for the above reactions, although it is noted that weight gains were generally observed at much higher temperatures. Equation 16 is the same as that postulated to occur with molten carbonate eutectic[20] and proposed as a method of removing sulfur dioxide from stack gases. However, the further reaction of the sulfite initially formed (i.e., eq 10 or eq 8 plus eq 14), which presumably also occurs in a molten carbonate, would have to be taken into account if a system was designed for use with anything other than a very large excess of carbonate.

Metabisulfite. Since metabisulfite can be cited as a reaction intermediate (see eq 7 and 10), its behavior was also investigated directly. Sodium metabisulfite in a nitrogen atmosphere, either heated alone or heated with ternary sulfate eutectic, gave a smooth weight loss from 160 to 210 °C of 33.2%, corresponding to the loss of sulfur dioxide (Figure 7, curves A and B).

$$Na_2S_2O_5 \rightarrow Na_2SO_3 + SO_2 \qquad \text{calcd wt loss 33.7\%} \qquad (18)$$

When air was admitted after the temperature had reached 700 °C, a weight gain (of 7.6 and 7.4%, respectively) was found. This corresponds closely to complete oxidation to sulfate (calculated weight gain for ${}^1/_2O_2$ per original $Na_2S_2O_5$ 8.4%) either in a direct manner, i.e. eq 13, or, more probably, after disproportionation, i.e. eq 8. In contrast, potassium metabisulfite, either heated alone or heated with sulfate eutectic, gave an identical weight loss from 190 to 300 °C (Figure 7, curve C), with both sulfur and sulfur dioxide being detected. The weight loss was 22.0%, and no further weight change was found under either nitrogen or air atmospheres on heating to 900 °C. After cooling, the reacted melt was found to contain no oxidizable sulfur species, suggesting the sole reaction was

$$K_2S_2O_5 \rightarrow K_2SO_4 + {}^1/_2S + {}^1/_2SO_2 \qquad \text{calcd wt loss 21.6\%} \qquad (19)$$

as has been reported by Forster and Hamprecht.[19] However, later workers[21,22] have reported the main decomposition pathway to be eq 18. It therefore seems probable that small differences of impurity concentration, gas atmosphere, heating rate, etc. may affect the overall reaction stoichiometry, particularly so as this occurs entirely in the solid state, well below the melting point of the eutectic. If, as has been postulated (eq 7 and 10), metabisulfite was produced in solution as a reaction intermediate, it seems reasonable that it should decompose as in eq 19, particularly as in the presence of excess sulfite reaction 18 would be suppressed if it were in equilibrium.

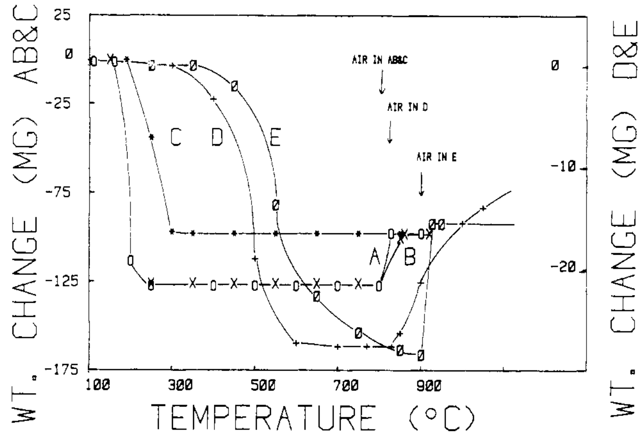

Figure 7. Thermogravimetric analysis of $Na_2S_2O_5$, $K_2S_2O_5$, and $Na_2S_2O_3$ by themselves and in Li_2SO_4–Na_2SO_4–K_2SO_4 eutectic under nitrogen and then air: A (○), $Na_2S_2O_5$ (0.38 g) alone; B (×), $Na_2S_2O_5$ (0.67 *m*) in 3 g of melt; C (*), $K_2S_2O_5$ (0.43 g) alone and 0.67 *m* in 3 g of melt; D (+), $Na_2S_2O_3$ (0.33 *m*) in 3 g of melt; E (⊘), $Na_2S_2O_3$ (0.16 g) alone.

Thiosulfate. When thiosulfate was heated with ternary eutectic, a weight loss commenced around 330 °C (Figure 7, curve D), reaching an equilibrium at 600 °C (total loss 17.4%) and suggesting the major reaction was probably

$$Na_2S_2O_3 \rightarrow Na_2SO_3 + S \qquad \text{calcd wt loss 20.2\%} \qquad (20)$$

No further loss occurred up to 830 °C though, when air was admitted, a gain of 8.5% was obtained, which similarly corresponds to the oxidation of sulfite (eq 13), giving a calculated overall weight loss of 10.1% based on the original $Na_2S_2O_3$, and certainly no oxidizable sulfur species were present at the end of the experiment. Once again, the sulfite is likely to have disproportionated (eq 8), and the sulfide produced, to have formed polysulfide, giving a lower loss of sulfur than predicted by eq 20. The corresponding gain on oxidation may have been lower because some sulfur voltailized as the polysulfides were converted to sulfate. Similar weight changes were found when thiosulfate was heated alone (Figure 7, curve E) but at generally higher temperatures, indicating the greater ease of re-

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action in solution and probably in the presence of lithium, the loss being 18.1% and the gain 8.2%. These results appear to be in accord with an earlier study in which thiosulfate was heated alone.[23] Sulfite, sulfate, polysulfide, and sulfur were all detected, although no simple stoichiometry was suggested to explain these products.

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Registry No. K_2SO_7, 7790-62-7; SO_4^{2-}, 14808-79-8; SO_3, 7446-11-9; NaCl, 7647-14-5; Cl_2, 7782-50-5; S, 7704-34-9; SO_2, 7446-09-5; Na_2SO_3, 7757-83-7; Na_2S, 1313-82-2; Na_2CO_3, 497-19-8; $Na_2S_2O_5$, 7772-98-7; $K_2S_2O_5$, 16731-55-8; $Na_2S_2O_3$, 7772-98-7; V_2O_5, 1314-62-1; CO_2, 124-38-9; nickel(II) sulfate, 7786-81-4; silica, 7631-86-9; polysulfide, 9080-49-3.

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Copper(I) and Copper(II) Chloro Complexes in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Ionic Liquid

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Potentiometry and absorption spectroscopy were used to study copper(I) and copper(II) chloro complex formation in the aluminum chloride–1-methyl-3-ethylimidazolium chloride ($AlCl_3$–MEIC) room-temperature ionic liquid. Analysis of data resulting from potentiometric titration experiments with the cell Al|$AlCl_3$–MEIC (66.7:33.3 mol %)|fritted disk|$AlCl_3$–MEIC, CuCl(dil)|Cu at 40, 60, and 100 °C indicated that copper(I) formed very stable, mononuclear chloro complexes of the type $CuCl_p^{1-p}$ in basic (chloride ion rich) compositions of this ionic liquid. At 40 °C, $CuCl_2^-$ and $CuCl_4^{3-}$ were the principal species. However, the relative fractions of these two complexes appeared to decrease in favor of $CuCl_3^{2-}$ as the temperature of the solvent was raised to 100 °C. Estimates of the stoichiometric formation constants for copper(I) chloro complexes in $AlCl_3$–MEIC are as follows. $CuCl_2^-$: 2.5×10^{23}, 40.0 °C; 2.6×10^{22}, 60.0 °C; 2.0×10^{19}, 100 °C. $CuCl_3^{2-}$: 1.0×10^{24}, 60.0 °C; 1.9×10^{21}, 100 °C. $CuCl_4^{3-}$: 9.2×10^{25}, 40.0 °C; 8.4×10^{24}, 60.0 °C; 1.2×10^{22}, 100 °C. Absorption spectra for copper(II) in basic $AlCl_3$–MEIC exhibited maxima at 293 and 407 nm. These spectra were very similar to those obtained for the unsolvated $CuCl_4^{2-}$ ion in *N*,*N*-dimethylformamide containing lithium chloride.

Introduction

Mixtures of aluminum chloride and either 1-*n*-butylpyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC) are ionic liquids at room temperature.[1,2] Both systems have been found to be good solvents for electrochemistry and spectroscopy. They are compatible with a wide variety of inorganic, organometallic, and organic solutes, and they are miscible with several molecular solvents like benzene, toluene, and acetonitrile. The Lewis acid–base properties of these ionic liquids can be varied by adjusting the ratio of $AlCl_3$ to organic salt. Melts in which the apparent mole fraction of $AlCl_3$ exceeds 0.5 are acidic, while those with an $AlCl_3$ mole fraction less than 0.5 are basic, since they contain uncomplexed chloride ion.

The comprehensive solvation properties of these melts with regard to transition-metal solutes have not been characterized to any extent. However, the results obtained during several studies suggest that some transition-metal cations exhibit a propensity to form stable, well-defined chloro complex anions in both basic $AlCl_3$–BPC and $AlCl_3$–MEIC. Cobalt(II), iron(II), iron(III), molybdenum(III), molybdenum(IV), nickel(II), and silver(I) chloro complexes have been identified in these melts.[3–8] Tetrahedral MCl_4^{n-4} chloro complexes were dominant for cobalt(II), nickel(II), iron(III), and iron(II).[3–6] Unsolvated $MoCl_6^{n-6}$ chloro complexes were found for molybdenum(III) and molybdenum(IV) in basic $AlCl_3$–MEIC.[7] Silver(I) formed several different mononuclear complexes, e.g., $AgCl_p^{1-p}$ ($2 \leq p \leq 4$), in basic $AlCl_3$–BPC and $AlCl_3$–MEIC melts. At 40 °C, $AgCl_2^-$ and $AgCl_4^{3-}$ were the predominant complex species, but $AgCl_3^{2-}$ became important as the temperature of the solvent was increased.[8]

No previous study of the solvation or complexation of copper(I) and copper(II) in room-temperature chloroaluminate ionic liquids appears in the literature. However, potentiometric studies indicate that copper(I) is complexed as $CuCl_2^-$ in molten $AlCl_3$–NaCl at 175 °C with a stability constant of 6.5×10^4.[9] Spectroscopic studies of copper(II) in molten LiCl–KCl were interpreted in terms of tetrahedral and tetragonally distorted tetrahedral $CuCl_4^{2-}$ species.[10–12] Copper(II) absorption spectra in molten $AlCl_3$ indicated octahedral coordination by two $Al_2Cl_7^-$ groups.[13] Copper(I) and copper(II) chloro complex formation has been studied extensively in nonaqueous organic solvents containing extrinsic chloride ion. CuCl and $CuCl_2^-$ are the principal copper(I) species usually found in these solvents, while $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^-$ are examples of copper(II) complexes that have been identified.[14–16] In the present study we have examined chloro

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